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(54) Title: PROCESS FOR THE PRODUCTION OF METALLIC TITANIUM AND INTERMEDIATES USEFUL IN THE PROCESSING OF ILMENITE AND RELATED MINERALS (57) Abstract <p>The invention relates to a process for the production of metallic titanium, characterized in that the process comprises reducing a titanium-fluorine compound selected from titanium tetrafluoride and any hexafluorotitanate soluble in a molten fluoroaluminate, with metallic aluminium in a molten fluoroaluminate. A process for the production of intermediates useful in the processing ilmenite and related minerals is also described.</p>		

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**PROCESS FOR THE PRODUCTION OF METALLIC TITANIUM
AND INTERMEDIATES USEFUL IN THE PROCESSING OF ILMENITE
AND RELATED MINERALS**

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This invention relates to a process for the production of metallic titanium and intermediates useful in the processing of ilmenite and related minerals.

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Australia is the major world producer of ilmenite which is exported for about A\$75 per tonne. The cost of metallic titanium in ingot form is about A\$20,000 per tonne. In a more refined form, for example, as the titanium-based alloy from which jet engine fan blades are fabricated, the value of metallic titanium is very much greater. Metallic titanium is, by comparison with most other metals and alloys, very resistant to chemical corrosion and is in great demand in the manufacture of chemical plants and for heat-exchangers and other units in power plants. Another important application is the use of metallic titanium in surgical and dental implants and supports. On a strength-for-weight basis, metallic titanium is stronger than steel and is widely used in the construction of supersonic military aircraft. A cheaper manufacturing route to the production of titanium would make feasible its use in civil aircraft to replace aluminium alloys which have proved to be subject to fatigue failure. This is one of the many applications in which the light, strong and non-corrosive metallic titanium would find wide commercial usage, if available more cheaply than from current processes.

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Currently, metallic titanium is produced commercially by two closely related processes. Titanium tetrachloride (TiCl_4) is reduced by either metallic sodium (Na) or magnesium (Mg). Each process yields an initial material called "titanium sponge" which may contain 10 to 20% of sodium chloride (NaCl) or magnesium chloride (MgCl_2) as products of the initial reaction. To avoid inclusion in the sponge of chlorides of titanium in lower oxidation states (e.g. TiCl_2 or TiCl_3), excess reducing metal (Na or Mg) is also in the sponge. Both methods of production are batch processes and the sponge, on solidification after reaction, must be removed from the reactor manually. It is reported that jack-hammers and even explosives are used. The sponge is then purified at least three times by vacuum arc-melting. The processes are both labour and energy intensive.

We have now found that a free-flowing powder of metallic titanium can be produced by employing a process which is similar to conventional aluminium smelting.

According to the present invention there is provided a process for the production of metallic titanium, characterized in that the process comprises reducing a titanium-fluorine compound selected from titanium tetrafluoride and any hexafluorotitanate soluble in a molten fluoroaluminate, with metallic aluminium in a molten fluoroaluminate.

The preferred titanium-fluorine compound is an alkali hexafluorotitanate, more preferably, sodium hexafluorotitanate (Na_2TiF_6) or potassium hexafluorotitanate (K_2TiF_6).

Preferably the molten fluoroaluminate is a hexafluoroaluminate, more preferably, cryolite (Na_3AlF_6).

In one particular embodiment of the invention, sodium hexafluorotitanate (Na_2TiF_6) or potassium hexafluorotitanate (K_2TiF_6) is dissolved in cryolite (Na_3AlF_6) at about 1000 to 1100 °C and metallic aluminium (Al) is added. Aluminium is chosen as the reductant because it is compatible with the melt, being oxidized in the first instance to aluminium fluoride (AlF_3) and then interacting with sodium fluoride (NaF) to form cryolite (Na_3AlF_6). In addition, aluminium is much less energy-intensive and cheaper to produce than sodium or magnesium reductants used in the current processes.

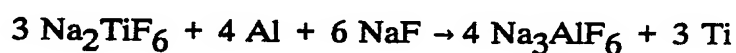
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Recovery of metallic titanium is achieved as a consequence of the relative densities of the reactants and the molten medium. Aluminium is less dense than cryolite which, in turn, is less dense than metallic titanium. Therefore, metallic titanium has a tendency to collect at the bottom of the reaction bath and may be tapped from that position with molten cryolite.

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The overall reaction for the reduction of Na_2TiF_6 by aluminium to metallic titanium in cryolite occurs in accordance with the equation:

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The pure compound Na_3AlF_6 constitutes a neutral molten medium. If the melt is deficient in NaF, i.e. contains an excess of AlF_3 , the medium is acidic. If the melt contains an excess of NaF, then the medium is basic.

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Na_2TiF_6 may be reduced by aluminium to metallic titanium directly in acidic or basic cryolite i.e. the direct reduction from Ti(IV) to Ti(0) may occur. However, the ultimate reduction to the metal is preferably carried out in neutral cryolite. Under neutral conditions Ti(IV) needs to be reduced only to Ti(II), which will disproportionate spontaneously in neutral medium according

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to the following equation:



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Metallic titanium i.e. Ti(0) is produced, and the Ti(IV) regenerated by the disproportionation reaction is available for reduction by aluminium to Ti(II) and subsequent disproportionation. This cyclic process continues until all Ti(IV) is reduced to Ti(0).

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Advantageously Na_2TiF_6 is added progressively to the cryolite bath in order to minimise loss of volatile TiF_4 which might result from thermal decomposition of Na_2TiF_6 . Sodium fluoride (NaF) may be added with Na_2TiF_6 preferably in the ratio 2:1 in order to maintain neutrality of the molten cryolite in accordance with the above equation. Aluminium may be added in a stoichiometric amount or in excess.

It will be appreciated that the process of the present invention may form the basis of a continuous process similar to that used for aluminium smelting. In one approach Na_2TiF_6 , Al and NaF may be added to the cryolite medium, in which case the product of the reaction is cryolite itself. A mixture of molten cryolite and the suspended metal may then be tapped from the bottom of the reactor. The solid material produced may then be crushed and initial separation of cryolite and titanium metal carried out by any suitable known technique, for example, flotation or cyclone separation. Any cryolite remaining attached to the titanium metal particles may be dissolved away from the titanium metal using any solution based on a metal cation which will complex with fluoride ions, preferably a solution of a water soluble aluminium compound, such as a solution of aluminium nitrate.

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Since the process of the present invention is similar to conventional aluminium smelting, an alternative procedure of electrowinning may be used in which Na_2TiF_6 and AlF_3 are added continuously to a cryolite bath, Ti being deposited at a graphite cathode. Advantageously a sacrificial anode reaction
5 could be utilized. AlF_3 would need to be added in the correct stoichiometric amount relative to Na_2TiF_6 (4:3) in order to maintain neutrality in the cryolite.

The feedstock for the process of the present invention is preferably
10 K_2TiF_6 or Na_2TiF_6 . It will be understood however that other sources of titanium may be used, such as, TiF_4 . A major disadvantage of TiF_4 is that it reacts readily with atmospheric moisture to form hydrogen fluoride and is difficult and dangerous to handle, whereas Na_2TiF_6 and K_2TiF_6 are stable in moist air and safe and easy to handle.

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We have now developed a process for the safe and easy conversion of TiF_4 to K_2TiF_6 or Na_2TiF_6 . In its broadest aspect, this process may be used for the production of intermediates useful in the processing of ilmenite and related minerals.

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Further according to the present invention there is provided a process for the production of intermediates useful in the processing of ilmenite and related minerals, characterized in that the process comprises:

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- a) dissolving a metal fluoride compound in an organic solvent;
- b) adding an ammonium fluoride to the metal fluoride compound dissolved in the organic solvent in step a) to precipitate an ammonium fluorometallate from the organic solvent; and

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- c) dissolving the ammonium fluorometallate from step b) in water and adding an alkali fluoride to produce an alkali fluorometallate and an ammonium fluoride.

5 The related minerals may include, for example, other titaniferous ores such as rutile, titaniferous slags or zircon.

 The organic solvent from step b) may be optionally recycled to step a) and the ammonium fluoride from step c) may be optionally recycled to step b).

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 Preferably the metal fluoride compound in step a) is selected from titanium tetrafluoride, zirconium tetrafluoride and tin tetrafluoride.

 The metal fluoride compound in step a) is often contaminated with an
15 impurity such as a metal oxidefluoride, for example, titanium oxidefluoride. As titanium oxidefluoride is insoluble in organic solvents, this impurity can be separated from the titanium fluoride compound by dissolving the mixture in an organic solvent. The metal oxidefluoride impurity remaining as a residue after treatment with the organic solvent can be heated to produce the desired metal
20 fluoride compound and a metal oxide. The metal oxide may then be treated to produce a metal oxide pigment or a refractory ceramic or recycled to produce metal fluoride compounds such as TiF_4 or ZrF_4 .

 The organic solvent in step a) is preferably an alcohol, such as, for
25 example, methanol or ethanol.

 Preferably the ammonium fluoride in step b) is selected from ammonium fluoride (NH_4F) or ammonium bifluoride (NH_4HF_2).

30 The ammonium fluorometallate produced in step b) may be ammonium fluorotitanate, such as, for example, ammonium hexafluorotitanate ($(\text{NH}_4)_2$

TiF₆ or ammonium fluorozirconate, such as, for example, ammonium heptafluorozirconate ((NH₄)₃ Zr F₇) and ammonium hexafluorozirconate ((NH₄)₂ ZrF₆). Preferably, the ammonium fluorometallate is ammonium hexafluorotitanate ((NH₄)₂ TiF₆) which may be used to produce K₂TiF₆ or Na₂TiF₆ which is the preferred feedstock employed in the process for the production of metallic titanium described above.

Preferably the alkali fluoride in step c) is potassium fluoride (KF) or sodium fluoride (NaF).

The alkali fluorometallate produced in step c) may be K₂TiF₆ or Na₂TiF₆ which is the preferred feedstock employed in the process for the production of metallic titanium described above.

In an alternative process, water and optionally base is added to the metal fluoride compound dissolved in the organic solvent in step a) to produce a hydrated metal oxide.

The hydrated metal oxide product from the alternative process may be treated to produce a metal oxide pigment or a refractory ceramic.

In a further alternative process, the ammonium fluorometallate from step b) is pyrohydrolysed to produce a hydrated metal oxide, an ammonium fluoride and hydrogen fluoride.

The ammonium fluoride may be optionally recycled to step b).

The hydrogen fluoride may be optionally treated with silicon dioxide and an alkali fluoride to produce an alkali fluorosilicate. The alkali fluorosilicate may then be heated to produce silicon tetrafluoride and an alkali fluoride. The silicon tetrafluoride may be optionally recycled for use in the

process for the formation of TiF_4 from minerals such as ilmenite and the subsequent conversion of TiF_4 to TiO_2 as described in our co-pending Australian Patent Application No. 48186/90.

5 The further alternative process may be performed using any suitable pyrohydrolysis technique. In a particularly preferred embodiment, a flow system having air with entrained water vapour may be streamed over a bed of the ammonium fluorometallate at temperatures sufficiently low to prevent sublimation of, for example, TiF_4 from a fluorotitanate ($200\text{-}300^\circ\text{C}$) or ZrF_4
10 from a fluorozirconate ($450\text{-}500^\circ\text{C}$). After an appropriate reaction time, typically 4 to 5 hours, the residues are hydrated TiO_2 or ZrO_2 . Volatile HF and NH_4F are carried out of the reaction zone in the air stream and may be condensed to form solid NH_4F and an aqueous solution of HF. The solid NH_4F may be optionally recycled to step b). The HF may be treated with
15 SiO_2 and KF or NaF to form K_2SiF_6 or Na_2SiF_6 which may be recovered and heated to about 600 to 700°C to yield SiF_4 which is recycled to a mineral reactor bed to produce further TiF_4 and ZrF_4 as disclosed in Australian Patent Application No. 48186/90. The KF or NaF residues may be recycled to step c). 100% recovery of TiO_2 or ZrO_2 and all of the fluoride in the
20 compounds volatilized during pyrohydrolysis has been demonstrated experimentally for pyrohydrolysis of $(\text{NH}_4)_2\text{TiF}_6$ and $(\text{NH}_4)_3\text{ZrF}_7$ under such conditions.

 The TiO_2 and ZrO_2 produced by the pyrohydrolysis in the further
25 alternative process are hydrated and therefore more chemically reactive than the TiO_2 and ZrO_2 obtained from conventional processes. In the conventional processing of ilmenite and related minerals such as zircon, high-temperature oxidation or hydrolysis reactions are used to convert intermediates into titanium dioxide (TiO_2) or zirconium dioxide (ZrO_2). In the chloride process
30 for pigment-grade TiO_2 production, titanium tetrachloride (TiCl_4) is burned in oxygen above 1000°C to produce TiO_2 . In the conventional production of

ZrO₂, zircon is fused with alkaline materials at about 1000 °C and then leached with aqueous solution. Sometimes the zircon is pre-heated by plasma techniques to about 2000 °C before leaching. As a result the TiO₂ and ZrO₂ products obtained in these conventional processes are refractory not
5 particularly amenable to subsequent purification or other processing.

Still further according to the present invention there is provided a process for the production of an intermediate useful in the processing of ilmenite and related minerals characterized in that the process comprises
10 producing an aqueous solution of a titanium or zirconium compound soluble in water or capable of reacting with water and adding an alkali fluoride and optionally excess fluoride to the aqueous solution to produce an alkali fluorotitanate or an alkali fluorozirconate.

15 The source of excess fluoride may be hydrogen fluoride or alkali fluoride.

The titanium compound capable of reacting with water in the further alternative process is preferably TiCl₄ which is produced in the chloride
20 pigment process described above. Preferably, the titanium compound soluble in water in the further alternative process is TiOSO₄ which is the intermediate produced in the sulphate pigment process. Both of these compounds may be used to produce K₂TiF₆ or Na₂TiF₆ which is the preferred feedstock employed in the process for the production of metallic titanium described
25 above. An example of zirconium compound capable of reacting with water is ZrCl₄.

The invention is further described in and illustrated by the following Examples. These Examples are not to be construed as limiting the invention
30 in any way.

Example 1

A mixture of about 30g Na_3AlF_6 and 1.9g of K_2TiF_6 was melted at 1090°C in a graphite crucible with a loose-fitting graphite lid. The inert gas argon was bubbled through a graphite lance dipping into the melt. A total of 0.28g of Al and 0.67g of NaF was added during the reaction by introducing several small compressed pellets of Al and NaF through the lance. After a period of settling, the melt was returned to room temperature and the graphite crucible was sectioned. A black powder was found to have settled towards the bottom of the solidified melt. When this black powder was washed free of cryolite with anhydrous hydrogen fluoride, the powder was shown by electron microprobe analysis to contain metallic titanium. Ignition of the black powder in air produced white titanium dioxide. Aqueous aluminium nitrate solution was shown subsequently to be effective in dissolving the cryolite away from the black powder.

Example 2

3.60g of a commercial, crude sample of TiF_4 containing large amounts of titanium oxidefluoride as an impurity, was stirred for several hours in methanol. The resulting solution was separated from the white insoluble residue and added to a saturated solution of NH_4HF_2 in 250 ml of methanol. An insoluble white precipitate of $(\text{NH}_4)_2\text{TiF}_6$ was formed immediately. After filtration, washing with methanol and drying in air, the mass of $(\text{NH}_4)_2\text{TiF}_6$ was 5.10g, corresponding with an initial weight of 3.19g of TiF_4 in the crude starting sample.

This example demonstrates the ease of recovery of $(\text{NH}_4)_2\text{TiF}_6$ from TiF_4 and the efficiency of the separation by dissolution in methanol of TiF_4 from accompanying oxidefluorides.

Example 3

0.318g of $(\text{NH}_4)_2\text{TiF}_6$ produced as in Example 2 in 5 ml H_2O was added dropwise to a solution of 0.218g of KF in 1 ml of water, cooled in an ice bath. The gelatinous white precipitate formed was collected by filtration and washed with 5 ml of ice-cold water to remove KF. Drying at 105°C yielded 0.287g of anhydrous, pure K_2TiF_6 . The filtrate was reduced by boiling to one-third of its volume and cooled to 0°C . A second yield of 0.088g of K_2TiF_6 was collected. Overall, the conversion rate of $(\text{NH}_4)_2\text{TiF}_6$ to K_2TiF_6 was 97%. Under process conditions, product recovery could be optimised by using a solution saturated with K_2TiF_6 throughout.

Example 4

0.1232g of $(\text{NH}_4)_2\text{TiF}_6$ produced as in Example 2 was pyrohydrolyzed at $200\text{--}250^\circ\text{C}$ for 5 hours. The weight of hydrated TiO_2 after pyrohydrolysis was 0.0524g, representing a nominal recovery of 105%. When this material was dehydrated by calcining, the weight of TiO_2 was 0.0499g, representing 100.4% recovery. Analysis for total fluoride in the NH_4HF_2 sublimate and in the aqueous condensate containing HF indicated 99.3% recovery.

Example 5

Three pyrohydrolyses at $450\text{--}500^\circ\text{C}$ for periods of 4 to 5 hours of $(\text{NH}_4)_3\text{ZrF}_7$ produced in a similar manner to Example 2 resulted in indicated recoveries of 99%, 101% and 103% for ZrO_2 and 99%, 102% and 104% for total fluoride.

CLAIMS:

1. A process for the production of metallic titanium, characterized in that the process comprises reducing a titanium-fluorine compound selected from titanium tetrafluoride and any hexafluorotitanate soluble in a molten fluoroaluminate, with metallic aluminium in a molten fluoroaluminate.
2. A process as claimed in Claim 1, characterized in that the titanium-fluorine compound is an alkali hexafluorotitanate.
3. A process as claimed in Claim 2, characterized in that the alkali hexafluorotitanate is sodium hexafluorotitanate (Na_2TiF_6) or potassium hexafluorotitanate (K_2TiF_6).
4. A process as claimed in any one of the preceding claims, characterized in that the molten fluoroaluminate is a hexafluoroaluminate.
5. A process as claimed in Claim 4, characterized in that the hexafluoroaluminate is cryolite (Na_3AlF_6).
6. A process as claimed in Claim 4, characterized in that the hexafluoroaluminate is neutral cryolite (Na_3AlF_6).
7. A process for the production of intermediates useful in the processing of ilmenite and related minerals characterized in that the process comprises:
 - a) dissolving a metal fluoride compound in an organic solvent;
 - b) adding an ammonium fluoride to the metal fluoride compound dissolved in the organic solvent in step a) to precipitate an

ammonium fluorometallate from the organic solvent; and

- 5 c) dissolving the ammonium fluorometallate from step b) in water and adding an alkali fluoride to produce an alkali fluorometallate and an ammonium fluoride.

8. A process as claimed in Claim 7, characterized in that the organic solvent from step b) is recycled to step a).

- 10 9. A process as claimed in Claim 7 or Claim 8, characterized in that the ammonium fluoride from step c) is recycled to step b).

10. A process as claimed in any one of Claims 7 to 9, characterized in that the metal fluoride compound in step a) is selected from titanium
15 tetrafluoride, zirconium tetrafluoride and tin tetrafluoride.

11. A process as claimed in any one of Claims 7 to 10, characterized in that the organic solvent in step a) is an alcohol.

- 20 12. A process as claimed in Claim 11, characterized in that the alcohol is methanol or ethanol.

13. A process as claimed in any one of Claims 7 to 12, characterized in that the ammonium fluoride in step b) is selected from ammonium fluoride
25 (NH_4F) or ammonium bifluoride (NH_4HF_2).

14. A process as claimed in any one of Claims 7 to 13, characterized in that the ammonium fluorometallate produced in step c) is ammonium fluorotitanate or ammonium fluoro-zirconate.

15. A process as claimed in Claim 14, characterized in that the ammonium fluorotitanate is ammonium hexafluorotitanate $((\text{NH}_4)_2\text{TiF}_6)$.

16. A process as claimed in Claim 14, characterized in that the
5 ammonium fluorozirconate is selected from ammonium heptafluorozirconate $((\text{NH}_4)_3\text{ZrF}_7)$ and ammonium hexafluorozirconate $((\text{NH}_4)_2\text{ZrF}_6)$.

17. A process as claimed in any one of Claims 7 to 16, characterized
in that the alkali fluoride in step c) is potassium fluoride (KF) or sodium
10 fluoride (NaF).

18. A process as claimed in any one of Claims 7 to 15 or 17,
characterized in that the alkali fluorometallate produced in step c) is K_2TiF_6
or Na_2TiF_6 .
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19. A process as claimed in any one of Claims 7 or 10 to 12,
characterized in that water and optionally base is added to the metal fluoride
compound dissolved in the organic solvent in step a) to produce a hydrated
metal oxide.
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20. A process as claimed in any one of Claims 7, 8, 10 to 16,
characterized in that the ammonium fluorometallate produced in step b) is
pyrohydrolysed to produce a hydrated metal oxide, an ammonium fluoride and
hydrogen fluoride.
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21. A process as claimed in Claim 20, characterized in that the
ammonium fluoride is recycled to step b).

22. A process as claimed in Claim 20 or 21, characterized in that the
30 hydrogen fluoride is treated with silicon dioxide and an alkali fluoride to
produce an alkali fluorosilicate.

23. A process as claimed in Claim 22, characterized in that the alkali fluorosilicate is heated to produce silicon tetrafluoride and an alkali fluoride.

24. A process as claimed in Claim 23, characterized in that
5 the alkali fluoride is recycled to step c).

25. A process for the production of an intermediate useful in the processing of ilmenite and related minerals characterized in that the process comprises producing an aqueous solution of a titanium or zirconium compound
10 soluble in water or capable of reacting with water and adding an alkali fluoride and optionally excess fluoride to the solution to produce an alkali fluorotitanate or an alkali fluorozirconate.

26. A process as claimed in Claim 25, characterized in that the
15 titanium or zirconium compound capable of reacting with water is TiCl_4 or ZrCl_4 , respectively.

27. A process as claimed in Claim 25, characterized in that the titanium compound soluble in water is TiOSO_4 .
20

28. A process as claimed in any one of Claims 25 to 27, characterized in that the alkali fluoride is potassium fluoride (KF) or sodium fluoride (NaF).

25 29. A process as claimed in any one of Claims 25 to 27, characterized in that the alkali fluorotitanate produced is K_2TiF_6 or NaTiF_6

INTERNATIONAL SEARCH REPORT

I. CLASSIFICATION OF SUBJECT MATTER (if several classification symbols apply, indicate all)⁶

According to International Patent classification (IPC) or to both National Classification and IPC
Int. Cl.⁸ C22B 34/12, 5/04, C01G 19/04, 23/02, 25/04

II. FIELDS SEARCHEDMinimum Documentation Searched ⁷

Classification System

Classification Symbols

IPC

C22B 34/12, 5/04, 53/00, C01G 19/04, 23/02, 25/04

Documentation Searched other than Minimum Documentation
to the Extent that such Documents are Included in the Fields Searched ⁸

AU : IPC as above
JOPAL

III. DOCUMENTS CONSIDERED TO BE RELEVANT ⁹

Category [*]	Citation of Document, ¹¹ with indication, where appropriate of the relevant passages ¹²	Relevant to Claim No ¹³
X	US,A, 2785971 (KAMLET, J.) 19 March 1957 (19.03.57) See column 2 lines 47-55	(1-6)
X	DE,C, 407508 (WESTINGHOUSE LAMP COMPANY) 16 December 1924 (16.12.24) See page 3 lines 25-59 and page 2 line 102 to page 3 line 15	(1-6) (25,26,28,29)
A	US,A, 4468248 (MEGY, J.A.) 28 August 1984 (28.08.84) See claims 1-20	(1-29)
X	US,A, 4437888 (JECKER, G.) 20 March 1984 (20.03.84) See claims 1-28	(1-6)
(continued)		

^{*} Special categories of cited documents : ¹⁰

"A" Document defining the general state of the art which is
not considered to be of particular relevance
"E" earlier document but published on or after the
international filing date
"L" document which may throw doubts on priority claim(s)
or which is cited to establish the publication date of
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exhibition or other means
"P" document published prior to the international filing date
but later than the priority date claimed

"T" Later document published after the international
filing date or priority date and not in conflict
with the application but cited to understand the
principle or theory underlying the invention
"X" document of particular relevance; the claimed
invention cannot be considered novel or cannot be
considered to involve an inventive step
"Y" document of particular relevance; the claimed
invention cannot be considered to involve an
inventive step when the document is combined
with one or more other such documents, such
combination being obvious to a person skilled in
the art
"&" document member of the same patent family

IV. CERTIFICATION

Date of the Actual Completion of the International Search
1 June 1992 (01.06.92)

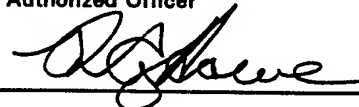
Date of Mailing of this International Search Report
4 June 1992 (04.06.92)

International Searching Authority

AUSTRALIAN PATENT OFFICE

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R. HOWE



FURTHER INFORMATION CONTINUED FROM THE SECOND SHEET

A	US,A, 2823991 (KAMLET, J.) 18 February 1958 (18.02.58) See column 2 lines 14-27	(1-6)
A	US,A, 2745735 (BYRNS, A.C.) 15 May 1956 (15.05.56) See claims 1-12	(1-6)
A	EP,A, 319857 (NKK CORPORATION) 14 June 1989 (14.06.89) See page 3 lines 16-24, example 1	(7)
X	US,A, 2717197 (BROWN) 6 September 1955 (06.09.55) See whole document	(25,26,28,29)
X	Derwent Abstract Accession No. 89-376969/51, Class E32, SU,A, 1465714 (RARE ELEMENTS MINER) 15 March 1989 (15.03.89)	(25,27-29)
X	Derwent Soviet Inventions Illustrated, Section 1, Chemical, Issued January 1967, 6: General Inorganic, etc, page 5, SU,A, 181638 (LOPATKINA et al) 13 June 1967 (13.06.67)	(25,27-29)

V. ☐ OBSERVATIONS WHERE CERTAIN CLAIMS WERE FOUND UNSEARCHABLE ¹

This international search report has not been established in respect of certain claims under Article 17(2)(a) for the following reasons:

- ☐ Claim numbers ..., because they relate to subject matter not required to be searched by this Authority, namely:
- ☐ Claim numbers ..., because they relate to parts of the international application that do not comply with the prescribed requirements to such an extent that no meaningful international search can be carried out, specifically:
- ☐ Claim numbers ..., because they are dependent claims and are not drafted in accordance with the second and third sentences of PCT Rule 6.4a

VI. ☒ OBSERVATIONS WHERE UNITY OF INVENTION IS LACKING ²

This International Searching Authority found multiple inventions in this international application as follows:

See attached sheet

- ☒ As all required additional search fees were timely paid by the applicant, this international search report covers all searchable claims of the international application.
- ☐ As only some of the required additional search fees were timely paid by the applicant, this international search report covers only those claims of the international application for which fees were paid, specifically claims:
- ☐ No required additional search fees were timely paid by the applicant. Consequently, this international search report is restricted to the invention first mentioned in the claims; it is covered by claim numbers:
- ☐ As all searchable claims could be searched without effort justifying an additional fee, the International Searching Authority did not invite payment of any additional fee.

Remark on Protest

- ☐ The additional search fees were accompanied by applicant's protest.
- ☒ No protest accompanied the payment of additional search fees.

III. DOCUMENTS CONSIDERED TO BE RELEVANT (CONTINUED FROM THE SECOND SHEET)

Category*	Citation of Document, ¹¹ with indication, where appropriate of the relevant passages ¹²	Relevant to Claim No ¹³
Y	Derwent Soviet Inventions Illustrated, Section I, Chemical, Issued 4 October 1973 (04.10.73) SU,A, 361980 (SHEKA et al) (Date in AU unknown)	(25)
X	Canterford, et al, "Halides of the Second and Third Row Transition Metals", published 1968, by John Wiley & Sons, Ltd, 31 December 1968 (31.12.68). See pages 128-129.	(25)

FURTHER INFORMATION CONTINUED FROM THE THIRD SHEET**VI. OBSERVATIONS WHERE ULNITY OF INVENTION IS LACKING (CONTD)**

The international application does not comply with the requirement of unity of invention for the following reasons:-

Claims 1-6 define a process for the production of metallic titanium by reducing titanium-fluorine compounds with metallic aluminium in a molten fluoroaluminate.

Claims 7-24 define a process for the production of alkali fluorometallate by dissolving a metallic fluoride compound in an organic solvent, adding an ammonium fluoride to the solution and dissolving the resultant ammonium fluorometallate in water and adding an alkali fluoride thereto.

Claims 25-29 define a process for the production of alkali fluorotitanate or alkali fluorozeirconate from alkali fluoride and aqueous solution of a titanium or zirconium compound.

Although there is some similarity between the last two sets of claims - both relate to the production of alkali fluorometallate from an aqueous solution of metal compounds and alkali fluoride - there is no link whatsoever between these claims on the one hand and claims 1-6 on the other hand. There is no common element of novelty or a single general inventive concept involved in the process of producing metallic titanium from e.g. TiF_4 by reduction with aluminium in a molten fluoroaluminate and the process of producing a totally different thing (alkali fluorometallate) by a totally different process (reaction in aqueous solutions).

**ANNEX TO THE INTERNATIONAL SEARCH REPORT ON
INTERNATIONAL APPLICATION NO. PCT/AU 92/00062**

This Annex lists the known "A" publication level patent family members relating to the patent documents cited in the above-mentioned international search report. The Australian Patent Office is in no way liable for these particulars which are merely given for the purpose of information.

Patent Document Cited in Search Report		Patent Family Member			
US	2785971				
DE	407508				
US	4468248				
US	4437888	CA 1163468 JP 58009949	EP 64903	FR 2505364	
US	2823991				
US	2745735				
EP	319857	AU 26351/88 US 4917872	BR 8806375 JP 1252531	EP 319857	
US	2717197				
SU	1465714				
SU	181638				
SU	361980				

END OF ANNEX